

# Error estimation in peak-shape analysis of XPS core-level spectra using UNIFIT 2003: how significant are the results of peak fits?

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**An error analysis for numerically evaluating random uncertainties in x-ray photoelectron spectroscopy has been implemented in version 2003 of the spectra treatment and analysis software UNIFIT in order to improve the understanding of the statistical basis and the reliability of the model parameters for photoelectron spectra. The theoretical basis as well as two approaches to obtain error limits of the fit parameters have been considered. Several test spectra have been analysed and discussed. A representative example has been chosen to demonstrate the relevance of the error estimation for practical surface analysis. Suggestions for the minimization of errors in the peak-fitting procedures are presented. Copyright © 2004 John Wiley & Sons, Ltd.**

**KEYWORDS:** UNIFIT; spectrum analysis software; photoelectron spectroscopy; peak fitting; data reduction; error analysis

## INTRODUCTION

Reliable surface analysis using core-level photoelectron spectra requires high-resolution spectrometers and spectra recording with a high counting rate and adequate preparation conditions. The analysis of monolayers and sub-monolayers benefits from the availability of synchrotron radiation sources with superior spectral resolution at appropriate beam lines and the additional advantage that the surface sensitivity of the photoelectron spectra can be tuned in a suitable manner. Nevertheless, careful analysis of the spectra<sup>1</sup> remains a challenge at every level of energy resolution of the spectra and therefore appropriate software<sup>2</sup> has to be employed to permit separation of close-lying spectral components and to derive reliable peak positions, intensities and other features. However, practical experience and comparing studies of the estimation of peak parameters from different test data with 20 participants<sup>3,4</sup> have shown that the component separation is often far from unique, particularly in the case of less-resolved minor components. In addition, Seah and Brown<sup>5,6</sup> studied the correctness of the generation of the Gaussian–Lorentzian product or sum model functions as well as the effectiveness of Shirley and Tougaard background subtraction of three spectrum processing programs using test spectra. The program UNIFIT<sup>2</sup> was tested extensively<sup>7</sup> with these suggested test data.<sup>6</sup> The Gaussian–Lorentzian product functions and the Shirley-background test function from Seah and Brown<sup>6</sup> were integrated in the software UNIFIT

to give the operator the possibility to carry out independent tests. Judgement by eye, analysis of residuals and the introduction of additional parameters to the fit may give some hints regarding the quality beyond the deviation  $\chi^2$  (see below). However, a statistical evaluation of the errors of the fit parameters is of increasing importance for the reliability of the quantitative analysis of the surface chemical state.

The measurement errors associated with calibration of the spectrometer and its analysis and detection modes, as well as errors from uncertainties in sensitivity factors, attenuation lengths, etc., will not be treated here. Generally, the inaccuracy of binding energies determined by means of thoroughly calibrated spectrometers is of the same order of magnitude as that of the peak-fitting procedure in the case of well-separated components. In contrast, the uncertainties in quantification of the sample composition by considering sensitivity factors, etc. may significantly exceed the standard deviation of the estimated peak areas from a fit of well-separated peaks.

This paper presents improvement to the software package UNIFIT<sup>2,7</sup> according to the suggestions made by Cumpson and Seah.<sup>8</sup> We have developed an additional sub-routine of the software to calculate the standard deviations of the adjustable parameters in order to provide error limits. Two methods—inversion of the Hessian matrix and an iterative estimation procedure for calculating the standard deviation of the peak parameters—are integrated in the software. The two different approaches are compared. Influences on the reliability of the peak fit will be studied by applying suitable examples.

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## THEORETICAL BACKGROUND

The program code UNIFIT offers two peak models (*product* and *convolution* of Gaussian and Lorentzian functions) to approximate a measured spectrum  $M(i)$  ( $i = 1 \dots N$ ;  $N$  = number of measurement points; see Eqns (2)–(6)<sup>2</sup>). The components of the model function are described using five parameters for the *product* (peak height, Gaussian–Lorentzian mixing ratio, energy, FWHM (full width at half-maximum), asymmetry) and five parameters for the *convolution* (peak height, Gaussian–FWHM, energy, Lorentzian–FWHM, asymmetry). In the case of a peak fit using  $Q$  components ( $q = 1 \dots Q$ ;  $Q$  = number of fitted components), five times  $Q$  parameters have to be optimized to find the minimum of  $\chi^2$  from Eqn. (1). If the background is approximated during the peak-fitting routine, the number of parameters may increase to six (see Eqn. 15). For example, a peak fit of a measured spectrum with four components ( $4 \times 5$  parameters) and a background consisting of three adjustable parameters, e.g. from a first-order polynomial plus a Shirley background, requires optimization of 23 fit parameters to find the minimum of the function  $\chi^2$  in Eqn. (1).

### Quantities for peak-fit evaluation and optimization

Most of the peak-fit software codes in use have implemented a numerical procedure to describe the measured spectrum  $M(i)$  by a set of model peaks  $S(i, \vec{p})$ , guided by the search for a minimum of  $\chi^2(\vec{p})$ , defined by<sup>2</sup>

$$\chi^2(\vec{p}) = \sum_{i=1}^N \frac{[M(i) - S(i, \vec{p})]^2}{M(i)} \quad (1)$$

where  $\vec{p}$  is a vector that includes the fit-parameter values,  $i$  indicates the  $i$ th data point in a spectrum and  $N$  is the total number of measured data points in the energy spectrum. Note that Eqn. (1) already includes the assumption that the error in  $M(i)$  may be represented by  $\sqrt{M(i)}$  according to the counting statistics. A reduced  $\chi^{2*}(\vec{p})$  may be defined by

$$\chi^{2*}(\vec{p}) = \frac{\chi^2(\vec{p})}{N - P} \quad (2)$$

where  $P$  is the number of independent parameters of the model function. In the case of purely statistical noise (Poisson-distributed intensities), the latter quantity should approach unity, i.e.  $\chi^{2*}(\vec{p}) \approx 1$ . Another quantitative measure describing correlations in the residuals and thus problems with the model functions is the so-called Abbe criterion, defined by

$$Abbe = \frac{1}{2} \frac{\sum_{i=1}^{N-1} [R(i+1) - R(i)]^2}{\sum_{i=1}^N [R(i)]^2} \quad (3)$$

with the residuals  $R(i) = S(i, \vec{p}) - M(i)$ . The calculated value of the Abbe criterion may indicate three limiting cases:

- 0 = systematically correlated residuals and therefore a bad choice of model function
- 1 = statistically distributed residuals and thus random noise

2 = systematically anti-correlated residuals, which is a reason to be suspicious

It is strongly recommended to include a normalized representation of the residuals  $R_N(i)$  in the presentation of the measured data together with the synthesized model spectrum (sum curve) and individual components

$$R_N(i) = \frac{S(i, \vec{p}) - M(i)}{\sqrt{M(i)}} \quad (4)$$

A statistically distributed  $R_N(i)$  may already be a strong hint for a reasonable outcome of the fitting procedure.

### Uncertainty of the fit parameters

With the approximation that  $\chi^2(\vec{p})$  is close to a parabolic form near the minimum in a plot of residuals in multi-parameter space, calculation of the uncertainty  $\Delta p_k$  of any parameter  $p_k$  from  $\vec{p}$ , with  $k = 1 \dots P$ , may be performed (as suggested by Bevington<sup>9</sup>). If we change one parameter  $p_k$  by an amount  $\Delta p_k$  and optimize all other parameters  $p_{j \neq k}$  to minimize  $\chi^2$ , then the new value of  $\chi^2$  will exceed the old value by  $\Delta \chi^2(\Delta p_k)$

$$\chi^2(p_k + \Delta p_k) = \chi^2(p_k) + \Delta \chi^2(\Delta p_k) \quad (5)$$

with

$$\Delta \chi^2(\Delta p_k) = n^2 \quad (n = 1, 2, 3, \dots) \quad (6)$$

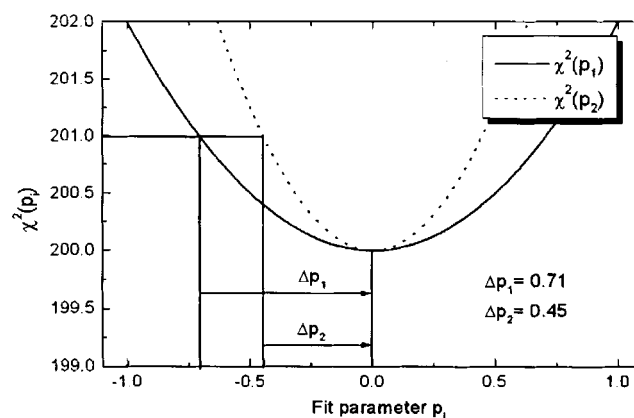
The uncertainty  $\Delta p_k$  becomes identical to the  $n$ -fold standard deviation  $\sigma(p_k)$  of the parameter  $p_k$ . Figure 1 displays two parabolic functions  $\chi^2(p_1)$  and  $\chi^2(p_2)$  of different curvature around their minima in the one-dimensional case and the related uncertainties  $\Delta p_1$  and  $\Delta p_2$ .

Evaluation of the standard deviation  $\sigma(p_k)$  starts from a Taylor expansion of Eqn. (5) limited to second order

$$\chi^2(p_k + \Delta p_k) = \chi^2(p_k) + \left. \frac{\partial \chi^2}{\partial p_k} \right|_{p_{k0}} \Delta p_k + \frac{1}{2} \left. \frac{\partial^2 \chi^2}{\partial p_k^2} \right|_{p_{k0}} (\Delta p_k)^2 \quad (7)$$

The first derivative is expected to vanish at the minimum of  $\chi^2$  and therefore with Eqn. (5) and  $n = 1$  we obtain

$$\chi^2(p_k) + 1 = \chi^2(p_k) + \frac{1}{2} \left. \frac{\partial^2 \chi^2}{\partial p_k^2} \right|_{p_{k0}} \sigma^2(p_k) \quad (8a)$$



**Figure 1.** Two functions  $\chi^2(p_1)$  (solid line) and  $\chi^2(p_2)$  (dotted line) in one dimension and the corresponding errors  $\Delta p_1$  and  $\Delta p_2$ ; values are arbitrary.

and finally at  $p_k$

$$\sigma(p_k) = \sqrt{\frac{2}{\left(\frac{\partial^2 \chi^2}{\partial p_k^2}\right)}} \quad (8b)$$

Thus, a large curvature of  $\chi^2(p_k)$  near a minimum results in a small standard deviation of the parameter  $p_k$  (see Fig. 1). However, this simplified treatment neglects the correlation of the parameters, and thus the correlations between the parameter uncertainties also should be determined. These may be included formally in the full matrix of second partial derivation  $\mathbf{H}$ , also called the Hessian matrix, which describes the curvature of  $\chi^2(\vec{p})$  in the multi-parameter space of  $\mathbf{P}$  parameters

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 \chi^2}{\partial p_1^2} & \frac{\partial^2 \chi^2}{\partial p_1 \partial p_2} & \cdots & \frac{\partial^2 \chi^2}{\partial p_1 \partial p_P} \\ \frac{\partial^2 \chi^2}{\partial p_2 \partial p_1} & \frac{\partial^2 \chi^2}{\partial p_2^2} & \cdots & \frac{\partial^2 \chi^2}{\partial p_2 \partial p_P} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 \chi^2}{\partial p_P \partial p_1} & \frac{\partial^2 \chi^2}{\partial p_P \partial p_2} & \cdots & \frac{\partial^2 \chi^2}{\partial p_P^2} \end{pmatrix} \quad (9)$$

This result is important when the Taylor expansion for  $\chi^2(\vec{p})$  is developed for a more general  $\Delta\vec{p}$ . The matrix  $\mathbf{H}$  is of key importance in the analysis of uncertainties of fit parameters.

The magnitude of the non-diagonal elements of  $\mathbf{H}$  compared with the diagonal elements provides a measure of correlations among the parameters of the peak model. Comparatively large non-diagonal elements indicate strong correlations that will result typically in large standard deviations and thus uncertainties of the corresponding parameters. In the case of completely independent parameters, the non-diagonal elements vanish and the problem of uncertainties may be reduced by applying Eqn. (8).

We have implemented two sub-programs for the peak-fit software UNIFIT, which permit calculation of the standard deviation  $\sigma(p_k)$  via either a matrix inversion or an iterative calculation.

#### Matrix inversion

The calculation of  $\sigma(p_k)$  is performed by numerical inversion of the matrix  $\mathbf{H}$  (Eqn. (9))

$$\mathbf{B} = \mathbf{H}^{-1} \quad (10)$$

Then, the standard deviation  $\sigma(p_k)$  is obtained from

$$\sigma(p_k) = \sqrt{2b_{kk}} \quad (11)$$

with  $b_{kk}$  taken from the appropriate diagonal elements of the error matrix  $\mathbf{B}$ . The UNIFIT code permits limits to be set for the parameters. In the case of  $p_k = p_{k,\min}$  or  $p_k = p_{k,\max}$ , it is assumed that  $\sigma(p_k) = 0$ . All parameters  $p_k$  that remain fixed during a minimum search also have their  $\sigma(p_k)$  fixed to zero.

#### Iterative calculation

This approach is based on a stepwise increase of  $\Delta p_k$  in order to form a test quantity for the increase of  $\chi^2(p_k)$  by  $p_k \rightarrow p_k + \Delta p_k$ . The starting value in this search progress for  $\Delta p_k$  is obtained by assuming independent parameters and

thus evaluating Eqn. (8) from the diagonal elements  $h_{kk}$  of Eqn. (9)

$$\Delta p_k = \sqrt{\frac{2}{h_{kk}}} \quad (12)$$

Note that in the case of a purely diagonal matrix  $\mathbf{H}$  the relation between  $h_{kk}$  and  $b_{kk}$  is determined by  $h_{kk}b_{kk} = 1$ . For any new calculation to determine a  $\chi_{new}^2$  after readjustment of  $p_k$  this parameter is kept fixed but all of the other parameters  $p_{j \neq k}$  are optimized to find the minimum in  $\chi^2(p_{j \neq k})$  for the particular choice of  $p_k$ . In the case of  $\chi_{new}^2$  with  $\chi_{new}^2 < \chi^2 + 1$  (see Eqn (5)),  $\Delta p_k$  is increased further and a new calculation for  $\chi_{new}^2$  is started until  $\chi_{new}^2 \geq \chi^2 + 1$ . This particular  $\Delta p_{k1}$  then corresponds to a first estimate of  $\sigma(p_k)$ . Because of the possible deviations from symmetric behaviour away from the minimum of  $\chi^2$ , the opposite direction is tested as well, resulting in a second estimate  $\Delta p_{k2}$ . The standard deviation  $\sigma(p_k)$  is identified to be the larger of these two values,  $\Delta p_{k1}$  and  $\Delta p_{k2}$ . This procedure has to be performed for all of the free parameters  $p_k$  of the fit model with  $k = 1 \dots P$ , until a standard deviation has been obtained for all free parameters. Note that in the present implementation in the UNIFIT code the parameter uncertainties are limited by the preset min/max values according to:

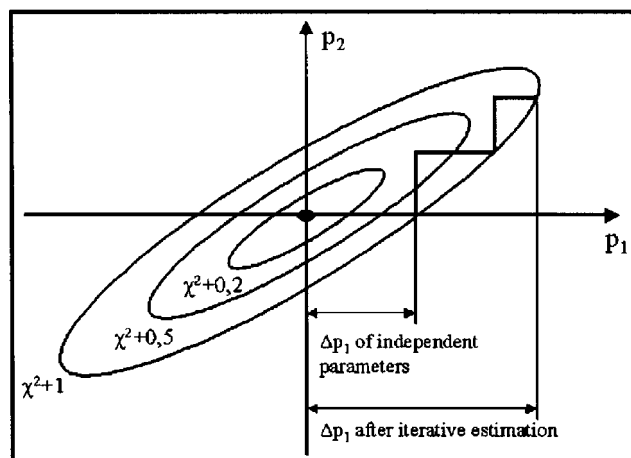
Case 1: if  $p_k - p_{k,\min} \leq p_{k,\max} - p_k$  and  $\Delta p_k \geq p_{k,\max} - p_k$ ,

then  $\sigma(p_k) = p_{k,\max} - p_k$

Case 2: if  $p_k - p_{k,\min} > p_{k,\max} - p_k$  and  $\Delta p_k \geq p_k - p_{k,\min}$ ,

then  $\sigma(p_k) = p_k - p_{k,\min}$

Figure 2 illustrates the above-described procedure for the simplified case of two free parameters. The origin is chosen to correspond to the minimum of the  $\chi^2(p_1, p_2)$  function. The tilting of the iso- $\chi^2$  lines with respect to the axes is due to correlation of the parameters. Independent parameters would result in iso-lines represented by ellipses



**Figure 2.** Illustration of the iterative calculation of  $\Delta p_1$  and  $\Delta p_2$ ;  $\chi^2(p_1, p_2)$  is a function of two dimensions and the ellipses are iso-lines of  $\chi^2(p_1, p_2)$ . The origin of the Cartesian coordinates represents the minimum of  $\chi^2(p_1, p_2)$  after a successful peak fit.

with main axes parallel to the axes of the Cartesian-parameter coordinate system. Lines indicate the stepwise approach to the correct  $\sigma(p_k)$  according to the outlined procedure. Note also that an assumption of independent parameters may result in a severe underestimate of the standard deviation and thus an incorrect surface analysis.<sup>8</sup>

### Calculation of the uncertainties of peak areas

The peak areas of fitted components  $A_q(\vec{p})$  are not explicit parameters in the UNIFIT software, and are calculated after the fitting process. Their maximum uncertainty  $\Delta A_q(\vec{p})$  consists of two parts:

- (1) the uncertainty that depends on the fitting parameters  $\Delta A_q^*(\vec{p})$  and the correlations among the peak-fit parameters, and
- (2) the error of the background estimated during the peak-fitting procedure  $\Delta A_q^{**}(\vec{p}_B)$  ( $\vec{p}_B$  background-parameter vector),

and is the sum of both

$$\Delta A_q(\vec{p}) = \Delta A_q^*(\vec{p}) + \Delta A_q^{**}(\vec{p}_B) \quad (13)$$

The uncertainty  $\Delta A_q^*(\vec{p})$  has to be derived from an equation that takes into account the uncertainties  $\Delta \vec{p}$  of all parameters according to:

$$\Delta A_q^* = |A_q(\vec{p} + \Delta \vec{p}) - A_q(\vec{p})| \quad (14)$$

with  $\Delta \vec{p} = \vec{\sigma}(\vec{p})$ .

The contribution of the background to the peak area uncertainty  $\Delta A_q^{**}(\vec{p}_B)$  is not included so far and is determined from the following procedure.

The most general description of the background  $B$  implemented in UNIFIT is

$$B(i, a, b, c, d, e, f) = a + bi + ci^2 + di^3 + eS(i) + fT(i) \quad (15)$$

where  $i$  is the channel number of the measured data points,  $S(i)$  is the Shirley background and  $T(i)$  is the Tougaard background. Typically, it is recommended to include the background function  $B$  in the fit procedure. In this case, the background parameters  $a$ – $f$  will be determined iteratively during the  $\chi^2$  minimization procedure.

The parameter vector  $\vec{p}_B$  can be represented by

$$\vec{p}_B = \begin{pmatrix} a \\ b \\ c \\ d \\ e \\ f \end{pmatrix} \quad (16)$$

giving an error of

$$\Delta B(i, \vec{p}_B) = |B(i, \vec{p}_B + \Delta \vec{p}_B) - B(i, \vec{p}_B)| \quad (17)$$

An individual background subtraction before the peak fit results in  $\Delta B(i, \vec{p}_B) = 0$ , but typically gives erroneous peak-fit results.<sup>2</sup>

Assuming that the background-corrected spectrum area  $A$  corresponds to

$$A = W_s \sum_{i=1}^N [M(i) - B(i, \vec{p}_B)] \quad (18)$$

where  $i$  is the channel number,  $W_s$  is the step width (in eV) and  $N$  is the total number of steps, the uncertainty of the spectrum area due to the background  $\Delta A$  is

$$\Delta A = W_s \sum_{i=1}^N \Delta B(i, \vec{p}_B) \quad (19)$$

The approximation currently used for the background contribution considers a weighting according to the relative peak areas of the fitted components compared with the total area of the spectrum. Thus the uncertainties of the peak area of fitted components  $\Delta A_q^{**}$  can be derived from the weighted contributions due to the background fit (Eqn. (19))

$$\Delta A_q^{**} = \frac{A_q}{A} \Delta A \quad (20)$$

## CALCULATION OF FIT-PARAMETER UNCERTAINTIES DEMONSTRATED FOR SYNTHESIZED TEST SPECTRA

### Generation of synthesized test spectra

In order to evaluate the calculated errors of the fit parameters, we have generated a series of eight test spectra reducing stepwise the separation of two components from 1.6 eV to 0.2 eV (see Fig. 3). The following parameters have been used to generate the test spectra:

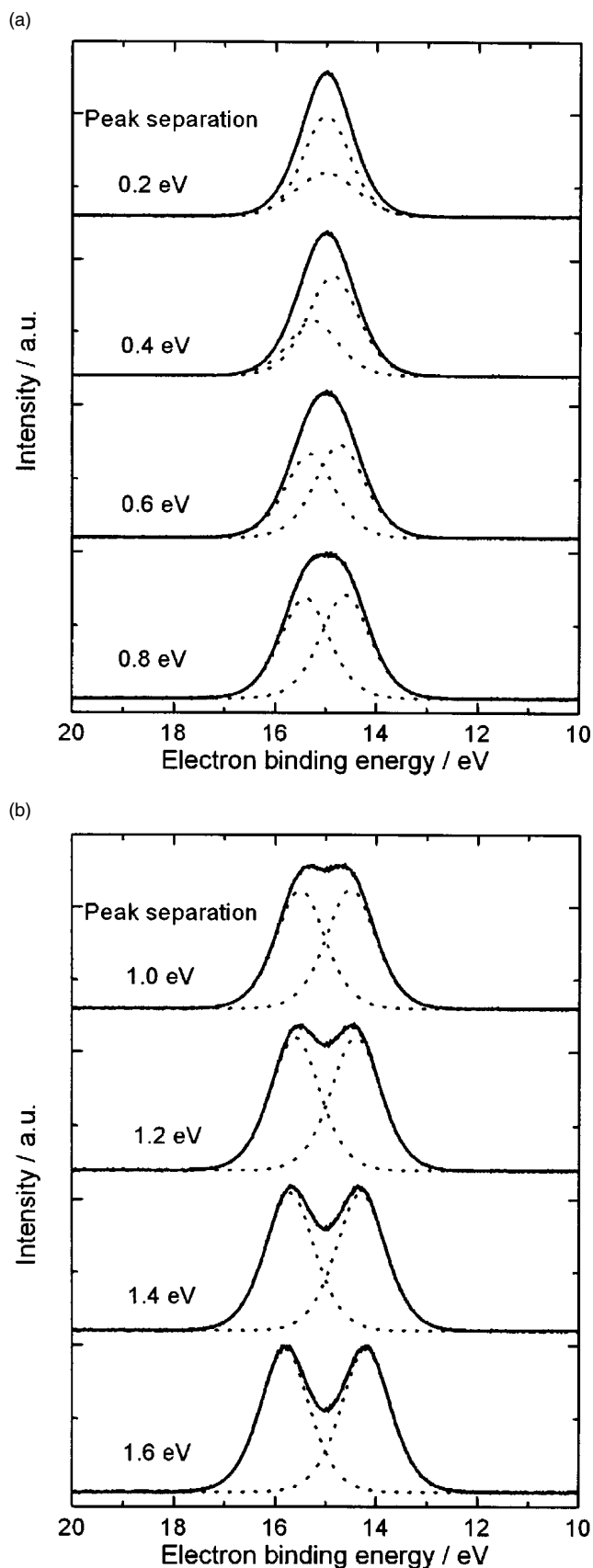
- (1) Product of Lorentzian and Gaussian lines, two components, arbitrary  $E_B$  range: 10–20 eV.
- (2) Intensities of both components: 10 000 counts.
- (3) Lorentzian–Gaussian ratio (L/G ratio): 0.5.
- (4) Peak width (FWHM): 1.2 eV.
- (5) Asymmetry: 0, fixed.
- (6) Background: constant, 1000 counts.
- (7) Line position component 1: 14.2–14.9 eV (spectra 1–8).
- (8) Line position component 2: 15.8–15.1 eV (spectra 1–8).

To each channel normally distributed noise was added with a standard deviation equal to the square root of the number of counts in that channel. For the generation of normally distributed noise the Box–Muller Polar method<sup>10</sup> was used.

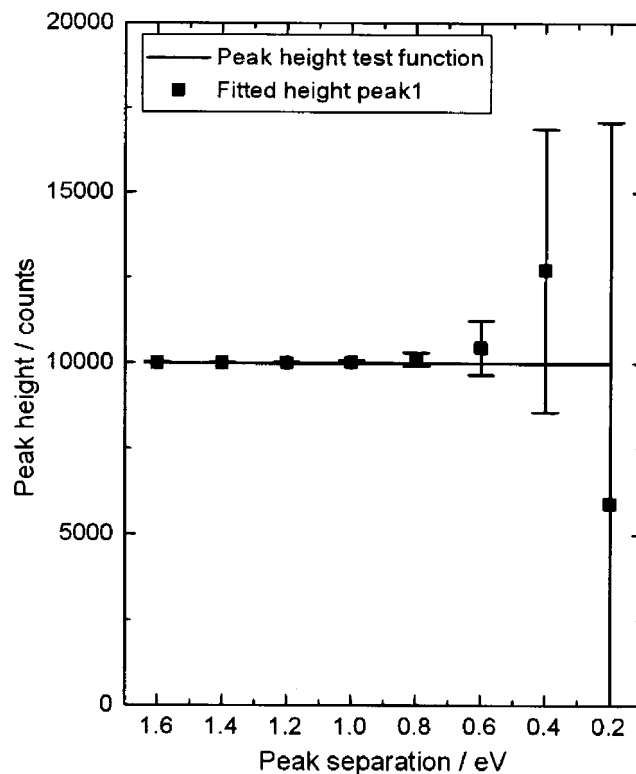
### Results of the peak fits and calculation of the uncertainties

All synthesized test spectra in Fig. 3 have been fitted, starting with initial values at least ~20% from the ideal value for the parameters, asymmetry parameters set to zero and kept fixed, no coupling of parameters, constant background determined together with the parameters of the model peaks in the fit and a number of peaks set to two. The following ranges for the control quantities  $\chi^2$ ,  $\chi^{2*}$  and the Abbe criterion were obtained

$$\chi^2 = 459\text{--}461, \quad \chi^{2*} = 0.939\text{--}0.941, \quad \text{Abbe} = 1.01\text{--}1.03.$$



**Figure 3.** Peak fits for synthesized test spectra, with the separation of the peaks reduced stepwise from: (a) 0.2 to 0.8 eV. (---) fitted components; (—) spectrum and sum curve; (b) 1.0 to 1.6 eV.



**Figure 4.** Illustration of the calculated peak heights for the first peak in Table 1 and in Fig. 3 and their errors; solid line at 10 000 counts gives the true intensities of the components of the test spectra.

In this test the calculation of the standard deviation of the parameters was performed using *matrix inversion*. In Fig. 4 peak heights of the first component as calculated during the fit and the corresponding uncertainties are displayed in order to represent the general behaviour of all fit parameters. Table 1 shows all the results of this test. In nearly all cases the true values fall within the estimated error margins of the determined parameter values (see also Fig. 4). However, in the case of peak separations smaller than 1/5 of the peak widths (FWHM) (peak separation = 0.2 eV), the calculated standard deviation may be too low because the  $\chi^2$  function is then rather flat near the minimum and possibly deviates from parabolic behaviour, the precondition for the definition of the parameter uncertainties (Eqn. (5)). Calculation of the standard deviation by *iterative calculation* gives rather similar results, with the exception of the spectrum with a peak separation of 0.2 eV (see Table 2). The standard deviation of the fitted peak positions estimated by iterative calculation seems more realistic in this case.

### Comparison of methods for the uncertainty evaluation

The method of matrix inversion ensures rather short calculation times for the uncertainties. However, numerical instabilities or other problems may prevent application of this method. For instance, if the iterative fit procedure did not arrive exactly at the minimum of  $\chi^2$  or in the case of very strong correlations of the fit parameters, which means that the non-diagonal elements of matrix  $H$  are large compared with the diagonal elements (the matrix may not be positively

**Table 1.** Fit parameters and calculated standard deviations using matrix inversion for the peak fit of the synthetic test spectra (Fig. 3)

Peak separation (eV)	Peak no.	Peak height (counts) Test spectra: 10 000	L/G ratio Test spectra: 0.5	Energy (eV)		FWHM (eV) Test spectra: 1.2	Peak area (cps · eV) Test spectra: 12 747
				Test spectra	Result		
				1.6	1		
	2	10 016 ± 23	0.509 ± 0.010	15.800	15.802 ± 0.002	1.198 ± 0.004	12 763 ± 102
1.4	1	10 000 ± 24	0.497 ± 0.011	14.300	14.301 ± 0.002	1.202 ± 0.005	12 766 ± 110
	2	10 002 ± 24	0.506 ± 0.011	15.700	15.702 ± 0.002	1.199 ± 0.005	12 752 ± 110
1.2	1	10 004 ± 27	0.493 ± 0.012	14.400	14.402 ± 0.003	1.204 ± 0.006	12 782 ± 129
	2	9 983 ± 27	0.504 ± 0.012	15.600	15.603 ± 0.003	1.200 ± 0.006	12 731 ± 130
1.0	1	10 024 ± 57	0.490 ± 0.014	14.500	14.504 ± 0.006	1.207 ± 0.009	12 828 ± 198
	2	9 943 ± 58	0.503 ± 0.014	15.500	15.404 ± 0.006	1.200 ± 0.009	12 680 ± 200
0.8	1	10 105 ± 200	0.486 ± 0.018	14.600	14.608 ± 0.012	1.211 ± 0.013	12 969 ± 444
	2	9 830 ± 205	0.503 ± 0.018	15.400	15.407 ± 0.012	1.200 ± 0.013	12 537 ± 445
0.6	1	10 451 ± 797	0.479 ± 0.026	14.700	14.721 ± 0.029	1.219 ± 0.022	13 490 ± 1356
	2	9 421 ± 828	0.505 ± 0.026	15.300	15.315 ± 0.029	1.199 ± 0.022	12 014 ± 1359
0.4	1	12 722 ± 4156	0.469 ± 0.036	14.800	14.866 ± 0.082	1.235 ± 0.040	16 616 ± 6274
	2	6 993 ± 4409	0.517 ± 0.058	15.200	15.253 ± 0.106	1.193 ± 0.050	8 887 ± 6386
0.2	1	5 892 ± 11 184	0.448 ± 0.070	14.900	14.997 ± 0.006	1.140 ± 0.161	9 080 ± 18 006
	2	13 672 ± 11 194	0.323 ± 0.290	15.100	15.007 ± 0.014	1.478 ± 0.341	16 426 ± 24 671

**Table 2.** Comparison of the calculated standard deviations of the fit parameters and peak areas using the different methods of matrix inversion (MatInv) and iterative calculation (IterCal) for the peak fit of the synthesized test spectra (Fig. 3)

Peak separation (eV)	Peak no.	Peak height (counts)		L/G ratio		Energy (eV)		FWHM (eV)		Peak area (cps · eV)	
		MatInv	IterCal	MatInv	IterCal	MatInv	IterCal	MatInv	IterCal	MatInv	IterCal
		1.6	1	±23	±29	±0.010	±0.011	±0.002	±0.002	±0.004	±0.005
	2	±23	±29	±0.010	±0.011	±0.002	±0.002	±0.004	±0.005	±102	±127
1.4	1	±24	±30	±0.011	±0.012	±0.002	±0.002	±0.005	±0.005	±110	±129
	2	±24	±30	±0.011	±0.011	±0.002	±0.002	±0.005	±0.005	±110	±129
1.2	1	±27	±30	±0.012	±0.018	±0.003	±0.003	±0.006	±0.007	±129	±161
	2	±27	±30	±0.012	±0.017	±0.003	±0.003	±0.006	±0.007	±130	±161
1.0	1	±57	±62	±0.014	±0.018	±0.006	±0.006	±0.009	±0.009	±198	±220
	2	±58	±62	±0.014	±0.017	±0.006	±0.006	±0.009	±0.009	±200	±220
0.8	1	±200	±210	±0.018	±0.023	±0.012	±0.012	±0.013	±0.014	±444	±479
	2	±205	±210	±0.018	±0.023	±0.012	±0.013	±0.013	±0.014	±445	±477
0.6	1	±797	±829	±0.026	±0.027	±0.029	±0.029	±0.022	±0.023	±1356	±1422
	2	±828	±857	±0.026	±0.028	±0.029	±0.030	±0.022	±0.024	±1359	±1426
0.4	1	±4156	±4627	±0.036	±0.040	±0.082	±0.091	±0.040	±0.043	±6274	±6990
	2	±4409	±4629	±0.058	±0.085	±0.106	±0.115	±0.050	±0.067	±6386	±6980
0.2	1	±11 184	±13 458	±0.070	±0.553	±0.006	±0.273	±0.161	±1.040	±18 006	±63 710
	2	±11 194	±13 648	±0.290	±0.678	±0.014	±2.698	±0.341	±3.522	±24 671	±88 933

definite), then diagonal elements of matrix  $B$  may become negative. In this case, calculation of the uncertainties is not possible by this method (see Eqn. (11)). Poor measurement statistics may result in estimates for the error of the parameters derived from matrix inversion that are too small.

The method of iterative calculation will result in satisfactory parameter errors in nearly all cases. The limits

according to the chosen min/max values of the parameters are considered exact. If the main fit procedure did not find the exact global minimum of  $\chi^2$  the iterative method introduced to the UNIFIT 2003 code might sometimes calculate a better  $\chi^2$  while estimating the fit parameter uncertainties compared with the original one. In these cases, the operator can apply the new improved fit parameters to start the fitting procedure

again to reach better results and a new  $\chi^2$ . In this case, the error calculation has to be repeated. The main problem with this approach is the extended computing time needed to determine the uncertainties. A large number of free parameters and huge parameter errors will increase the computing time enormously. Usually the computing time of the iterative method is about 30 times higher than that of the matrix inversion. In exceptional cases with very weak correlation of the parameters, the errors may be found to be too large. Note that during error estimation using the iterative method the operator can observe the variation of  $\chi^2$  and the fitting curves depending on modification of the adjustable parameters.

### FACTORS OF INFLUENCE FOR THE CORRECTNESS OF PEAK FITS

Several factors may affect the result of a peak fit for a measured spectrum using a set of parameterised model functions. The most important are:

- (1) Choice of an appropriate model function in order to improve the  $\chi^2$ .
- (2) Treatment of the spectral background.
- (3) Treatment of excitation satellites in non-monochromatized standard spectra that may not only depend on energies but also on the pass energy of analysers.
- (4) Consideration of existing information on intensity ratios and separations of doublets, chemically shifted components, etc.
- (5) The noise: signal-to-noise ratio (S/N), signal-to-background ratio (S/B) and noise distribution.

Recently, we have considered the first two of the above factors.<sup>1</sup> Now we will provide examples related to items 4 and 5.

#### Application of existing information

The minimum search of  $\chi^2$  is a rather complex iterative process because of the coupling and interdependence of

the parameters. Available information on peak positions or relative intensities may help to reduce the number of free parameters and put constraints on the fit. This approach may improve convergence and reduce the uncertainties of the peak parameters found in the peak fit.

An S 2p spectrum from two chemically shifted doublets may serve as an example. Figure 5 displays results of fits that were performed with slightly different constraints regarding the peak model. In case A all parameters were allowed to vary freely (except the asymmetry), whereas in case B the peak separation of the doublet lines (1.2 eV), the doublet Lorentzian–Gaussian mixing ratio (1:1) and the intensity ratio (2:1) were kept fixed. The background was included in the fit for both cases.

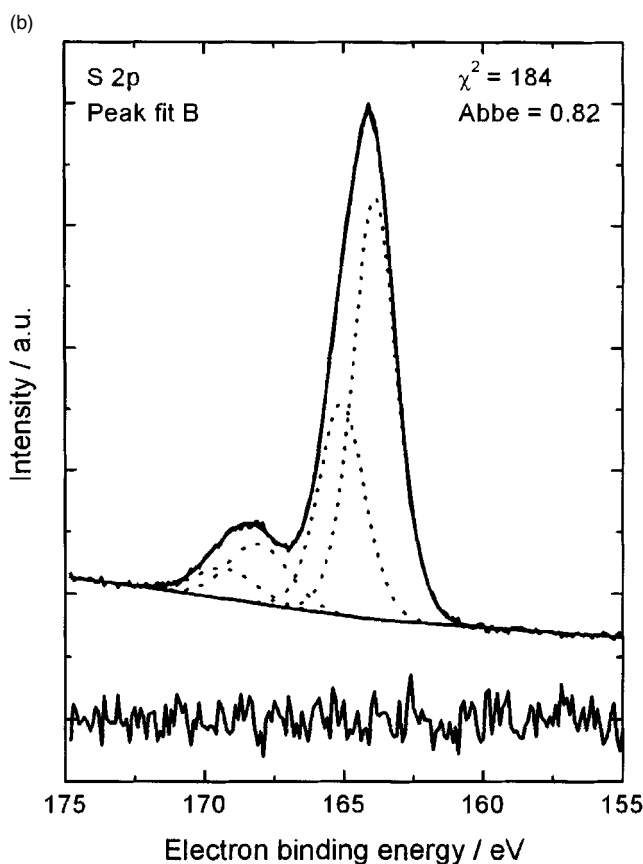
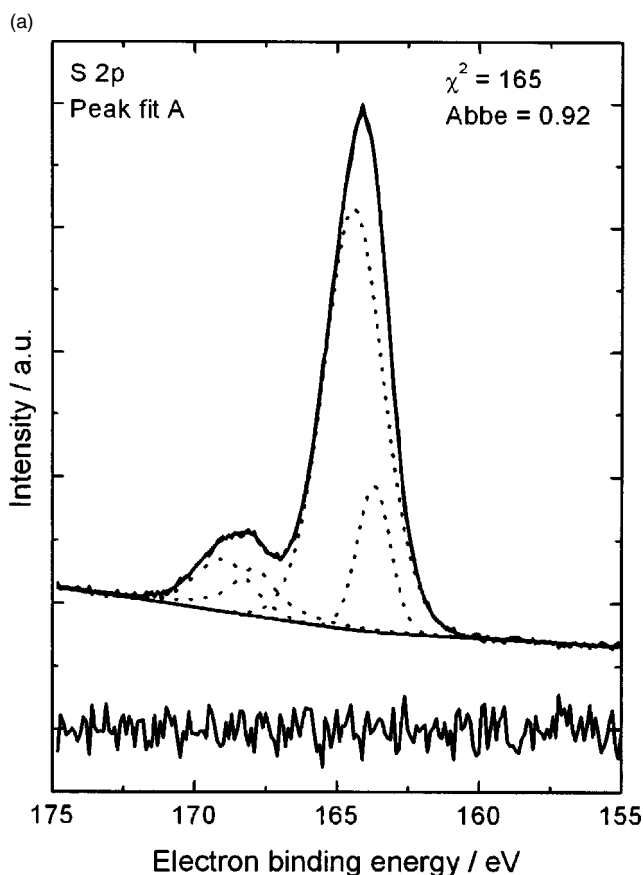
Both fits succeeded with a visually good representation of the experimental spectrum by the model peaks. The normalized residuals  $R_N(i)$  look like a random distribution in both cases, giving no indication of an incorrect result. Because the minimized quantity  $\chi^2$  is slightly smaller in case A ( $\chi^2 = 165$ ,  $\chi^{2*} = 0.92$ , Abbe = 0.92) compared with case B ( $\chi^2 = 184$ ,  $\chi^{2*} = 1.05$ , Abbe = 0.82), only the fit-parameter uncertainties as expressed by standard deviations elucidate the problem. Although the calculated errors of the energy positions in case A fall between 0.03 and 2.05 eV, they are between 0.01 and 0.03 eV in case B. A similar tendency is displayed for the uncertainties of the peak intensities. In case A the uncertainty of the peak areas is 21–290%. On the contrary, in case B the peak-area uncertainties are much smaller (6–32%) because of the reduced variabilities acting like constraints, making  $\chi^2$  steeper close to its minimum and thus reducing the uncertainties. All the determined parameters and uncertainties are summarized in Table 3.

#### Influence of noise in the spectrum

The noise and thus the statistical quality of the measured spectrum influence strongly the result of the fit procedure. A small signal-to-noise ratio or a large noise may lead to unreliable fit results and incorrect uncertainties.<sup>8</sup>

**Table 3.** Calculated parameters and their standard deviations for the fit to the S 2p spectrum in Fig. 5 with free doublet values (test A) and frozen doublet values (test B)

Line	Peak height (counts)		L/G ratio		Energy (eV)		FWHM (eV)		Peak area (cps · eV)	
	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
<i>Test A</i>										
Peak 1/1	2880	±362	0.001	±0.127	163.70	±0.03	1.36	±0.07	4161	±862
Peak 1/2	9055	±2515	0.345	±0.652	164.41	±0.52	2.59	±0.27	24 537	±24 637
Peak 2/1	1090	±369	0.578	±0.559	167.94	±0.16	1.93	±0.27	2262	±2477
Peak 2/2	1049	±975	0.503	±0.503	169.16	±2.05	2.39	±0.90	2665	±7733
Background $B(i) = (1749 \pm 13) + (3.6 \pm 0.4)i + (1.7 \pm 0.3)T(i)$ (see Eqn. (15))										
<i>Test B</i>										
Peak 1/1	9082	±58	0.510	±0.028	163.88	±0.01	1.91	±0.02	18 455	±1048
Peak 1/2	4541	±28	0.510	±0.028	165.08	±0.01	2.02	±0.05	9758	±714
Peak 2/1	1294	±48	0.422	±0.337	168.11	±0.03	2.49	±0.11	3390	±705
Peak 2/2	647	±24	0.422	±0.337	169.31	±0.03	2.47	±0.33	1681	±530
Background $B(i) = (1737 \pm 12) + (4.2 \pm 0.4)i + (1.4 \pm 0.2)T(i)$ (see Eqn. (15))										



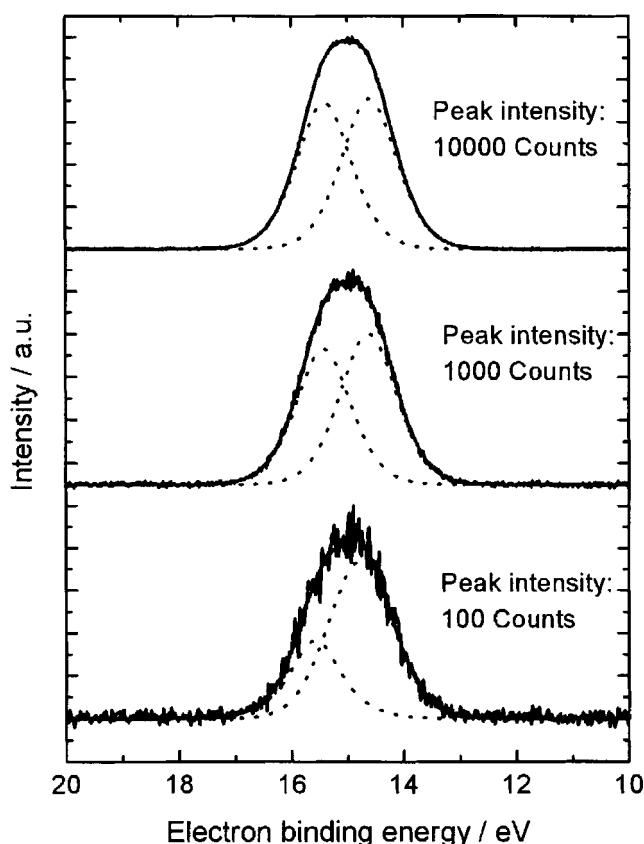
**Figure 5.** Illustration of the peak fit of an S 2p spectrum from two chemically shifted doublets: (a) with free doublet values (test A); (b) with frozen doublet values (test B). (---) fitted components; (—) spectrum and sum curve.

In order to test the influence of noise on fit parameters and standard deviations we have generated three synthetic spectra using the following parameters:

- (1) Product of Lorentzian and Gaussian lines, two components of equal intensity.
- (2) Arbitrary  $E_B$  range: 10–20 eV.
- (3) Lorentzian–Gaussian ratio (L/G ratio): 0.5.
- (4) FWHM: 1.2 eV.
- (5) Line separation: 0.8 eV.
- (6) Asymmetry: 0, fixed.

The peak separation of 2/3 of the FWHM was chosen to permit a successful fit as demonstrated above. Variation of the noise content was achieved by increasing the absolute intensities  $I_1$  and  $I_2$  of the two components, step by step, by an order of magnitude each (100 counts, 1000 counts, 10000 counts). The signal background was assumed to have 10% of the intensity of the individual lines, representing a signal-to-background ratio S/B of 10. The background then was simply added to the sum of the peaks and a normally distributed noise<sup>10</sup> was superimposed. All test spectra have been fitted using the same set of starting parameters.

The following values have been obtained for the control criteria values  $\chi^2$ ,  $\chi^{2*}$  and the Abbe criterion:  $\chi^2 = 460$ –547;  $\chi^{2*} = 0.95$ –1.12; Abbe = 0.98–1.02.



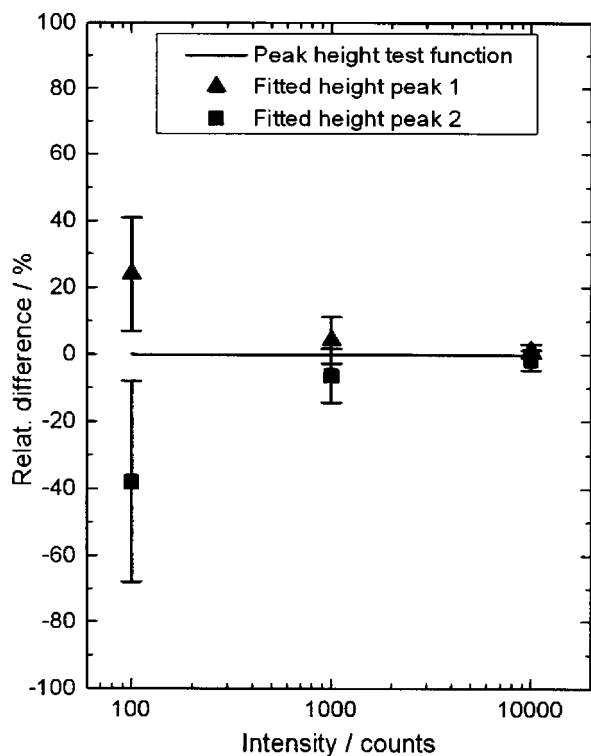
**Figure 6.** Illustration of a peak fit of three test spectra with different intensities of the two single peaks (100 counts, 1000 counts, 10000 counts) used to generate the spectrum: (---) fitted components; (—) spectrum and sum curve.

**Table 4.** Estimated fit parameters and standard deviations of three synthesized test spectra with variation of the noise level (see Fig. 6)

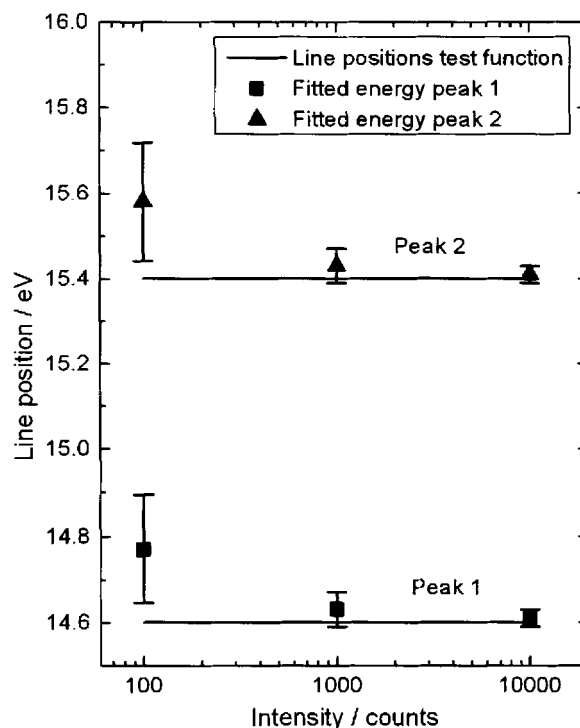
Peak no.	Peak height (counts)		L/G ratio		Energy (eV)		FWHM (eV)		Peak area (cps · eV)	
	Test spectra	Result	Test spectra	Result	Test spectra	Result	Test spectra	Result	Test spectra	Result
1	100	125 ± 17	0.50	0.29 ± 0.25	14.60	14.77 ± 0.13	1.20	1.40 ± 0.15	127	182 ± 53
2	100	62 ± 30	0.50	0.74 ± 0.19	15.40	15.58 ± 0.14	1.20	1.09 ± 0.15	127	77 ± 69
Background = (8.71 ± 0.20), $\chi^2 = 547$ , $\chi^{2*} = 1.12$ , Abbe = 0.98										
1	1000	1042 ± 68	0.50	0.45 ± 0.07	14.60	14.63 ± 0.04	1.20	1.24 ± 0.05	1274	1363 ± 158
2	1000	936 ± 76	0.50	0.52 ± 0.06	15.40	15.42 ± 0.05	1.20	1.20 ± 0.05	1274	1192 ± 161
Background = (99.06 ± 0.61), $\chi^2 = 465$ , $\chi^{2*} = 0.95$ , Abbe = 1.02										
1	10 000	10 105 ± 200	0.50	0.49 ± 0.02	14.60	14.61 ± 0.02	1.20	1.21 ± 0.02	12 744	12 969 ± 444
2	10 000	9830 ± 205	0.50	0.50 ± 0.02	15.40	15.41 ± 0.02	1.20	1.20 ± 0.02	12 744	12 537 ± 446
Background = (999.21 ± 1.94), $\chi^2 = 460$ , $\chi^{2*} = 0.95$ , Abbe = 1.02										

Estimation of the parameter uncertainties was performed using the matrix inversion method. Table 4 presents all calculated fit parameters and the corresponding uncertainties. Figure 6 shows a graphical presentation of the fit results. Peak heights and line positions have been chosen to represent all the parameters and are shown in Figs 7 and 8. Error bars indicate the determined standard deviations.

The inadequacies of the calculated parameters compared with the true parameters for the lowest intensity are quite obvious in Fig. 6. The S/N ratio is ~13 for the peak maximum



**Figure 7.** Presentation of the calculated peak heights for fits to the spectra of Fig. 6 as relative peak heights  $[(h_{\text{fit}} - h_{\text{true}})/h_{\text{true}}] \times 100\%$ . The estimated standard deviations are displayed as error bars; the solid line at 0% gives the true peak height of the test spectra.



**Figure 8.** Presentation of the calculated energies for fits to the spectra of Fig. 6. The estimated standard deviations are displayed as error bars; the solid lines at 14.6 and 15.4 eV give the true energies of the test spectra.

in this case. Interestingly, the peak parameter uncertainties evaluated by matrix inversion cannot alone account for the deviations between the calculated and true parameters. Note that the iterative procedure resulted in qualitatively very similar results. The noise distribution for this particular test example evidently gives a  $\chi^2$  minimum in parameter space quite different from that to be expected for the true parameter set without noise. The calculated uncertainties correspond to this minimum rather than the correct one, and thus suggest completely erroneous information to the operator. This example demonstrates what may accidentally happen if the noise is too large.

**Table 5.** Comparison of estimated errors of the peak areas listed in Table 4 calculated using Eqns (13) and (21)

Peak no.	Peak height for test peak (counts)	Peak area for test peak (cps · eV)	Results after peak fit (cps · eV)	Error in peak areas using Eqn. (13) (cps · eV)	Error in peak areas using Eqn. (21) (cps · eV)
1	100	127	182	±53	±44
2	100	127	77	±69	±48
1	1000	1274	1363	±158	±144
2	1000	1274	1192	±161	±146
1	10 000	12 744	12 969	±444	±471
2	10 000	12 744	12 537	±446	±470

The fit of the test spectrum with the intermediate intensity (1000 counts, S/N ~42) (see Fig. 6) results in reasonable agreement of the fit parameters to the test parameters, and the derived uncertainties ensure that nearly all true parameters fall into the error limits of the calculated parameters (Table 4). The relative errors of the peak areas are 12–14% and the uncertainty of the peak positions is ~0.3%. To obtain more reliable results a further improvement of the S/N is needed. This is demonstrated in the case of the last set of peaks with the highest intensities (10 000 counts, S/N ~135 for the peak maximum). The calculated parameters fall close to the expected ones and the uncertainties are much smaller compared with the previous example. Now uncertainties for the peak areas of ~4% are found and the relative errors for the peak positions are <0.14%.

Thus, the operator has to find a reasonable balance between the time needed for the measurement and the quality of the measurement statistics required to arrive at the uncertainty level needed for a satisfactory sample analysis. This balance has to be considered during the process of spectra recording. Harrison and Hazell<sup>11</sup> have suggested an optimized acquisition strategy to improve the reliability of the results.

In order to test the reliability of the results the estimated errors of the peak areas were compared to errors obtained using Eqn. (21) (see formula (A2.11)<sup>8</sup>). If the peak area  $A$  is proportional to the product of the FWHM  $w$  and the peak height  $h$ , the standard deviation  $\sigma_A$  of the associated peak area is given by

$$\sigma_A = A \frac{h\delta w + w\delta h}{wh} \quad (21)$$

where  $\delta w$  and  $\delta h$  are the estimated errors of the FWHMs and peak heights. This formula neglects influences of other peak-shape parameters. Table 5 shows that the results of using Eqns (13) and (21) are very close for our test example. Note that Eqn. (21) cannot be used in the case of Gaussian–Lorentzian convolution function peaks. Additionally, the uncertainty of the background  $\Delta B$  estimated during the peak-fitting procedure is neglected.

The conclusions are in good agreement with the recommendations given by Cumpson and Seah:<sup>8''</sup> In either case, avoid fits involving  $\leq 100$  counts per channel."

## FINAL DISCUSSION AND CONCLUSIONS

Although  $\chi^2$ ,  $\chi^{2*}$ , the Abbe criterion and the residuals are indispensable quantities for choosing a reasonable fit

model and guiding the procedure, further information with respect to the significance of the individual fit parameters is needed to evaluate the results of a fit. This information may be derived efficiently from calculations of parameter errors given by standard deviation. We have demonstrated the success of two different numerical approaches to such a goal, one being based on a matrix inversion and the other on an iterative procedure. Advantages and problems of both methods have been demonstrated and discussed. Implementation of both approaches in the software UNIFIT permits the operator to obtain peak-parameter uncertainties and to cross-check the results.

Further, we have particularly considered the importance and the benefit of inclusion of established knowledge in the peak model and the possible effects due to noise level on the peak parameters and their uncertainties.

In conclusion, a few recommendations may be derived from the above investigations of test cases as well as previous studies<sup>7</sup> and long-standing experience. The significance of the fit results and thus the sample analysis may benefit from the following recommendations:

- (1) Recording of spectra with low noise and high peak-to-background ratio.
- (2) Suitable choice of the model function (convolution of Lorentzian and Gaussian functions<sup>2</sup>, etc.).
- (3) Reducing the number of free parameters by means of existing information on well-known doublet splitting and intensity ratios.
- (4) Running the fit procedure with background included.
- (5) Checking the values of  $\chi^2$ ,  $\chi^{2*}$  and the Abbe criterion.<sup>7</sup>
- (6) Checking the distribution of normalized residuals for random behaviour.
- (7) Calculation and check of parameter errors.
- (8) Consideration of series of spectra recorded under similar conditions rather than an individual spectrum.

Further detailed treatment of the fit data based on statistical procedures as suggested by Leclerc and Pireaux<sup>12–14</sup> may shed additional light on the significance of the outcome of the fit procedure. However, this requires further elaborate and extensive numerical data treatments, that possibly may not be included routinely in an everyday data analysis. We have therefore confined ourselves to a pragmatic approach, which may nevertheless result in an improvement of the analysis.

## Acknowledgements

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## REFERENCES

1. Sherwood PMA. In *Practical Surface Analysis* (2nd edn), vol. 1, Briggs D, Seah MP (eds). John Wiley: Chichester; 1990; 555.
2. Hesse R, Chassé T, Szargan R. *Fresenius J. Anal. Chem.* 1999; **365**: 48; [www.uni-leipzig.de/~unifit](http://www.uni-leipzig.de/~unifit).
3. Conny JM, Powell CJ, Currie LA. *Surf. Interface Anal.* 1998; **26**: 939.
4. Conny JM, Powell CJ, Currie LA. *Surf. Interface Anal.* 2000; **29**: 444.
5. Seah MP, Brown MT. *Appl. Surf. Sci.* 1999; **183**: 144.
6. Seah MP, Brown MT. *J. Electron Spectrosc. Relat. Phenom.* 1998; **95**: 71.
7. Hesse R, Chassé T, Szargan R. *Anal. Bioanal. Chem.* 2003; **375**: 856; [www.uni-leipzig.de/~unifit](http://www.uni-leipzig.de/~unifit).
8. Cumpson PJ, Seah MP. *Surf. Interface Anal.* 1992; **18**: 345.
9. Bevington PB. *Data Reduction and Error Analysis for the Physical Sciences* (2nd edn). McGraw-Hill: New York, 1992.
10. Blobel V, Lohmann E. *Statistik und Numerische Methoden der Datenanalyse*. Teubner: Stuttgart, 1991; 166.
11. Harrison K, Hazell LB. *Surf. Interface Anal.* 1992; **18**: 368.
12. Leclerc G, Pireaux JJ. *J. Electron Spectrosc. Relat. Phenom.* 1995; **71**: 141.
13. Leclerc G, Pireaux JJ. *J. Electron Spectrosc. Relat. Phenom.* 1995; **71**: 165.
14. Leclerc G, Pireaux JJ. *J. Electron Spectrosc. Relat. Phenom.* 1995; **71**: 179.